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CRYSTALS NEAR THE PHASE TRANSITIONS

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Low Frequency Raman Mode in Smectic Liquid Crystals
Near the Phase Transitions

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ABSTRACT

A low-frequency intermolecular Raman mode at $\sim 24 \text{ cm}^{-1}$ was observed in the solid phase of two related smectic A compounds. This mode shifts abruptly to lower frequency and decreases in intensity at the transition to smectic, while vanishing in the liquid phase. Qualitative interpretation of the results is given.

Un mode Raman intermoleculaire de basse fréquence a été observé a 24 cm^{-1} , dans la phase solide de deux composés smectiques A. Ce mode se deplace soudainement vers les basses fréquences et décroît en intensité à la transition solide-smectique, tandis qu'il disparaît dans la phase liquide. On donne une interprétation qualitative des résultats.

We have investigated the Raman spectra of the smectic A¹ compounds diethylazoxybenzoate (DEAB) and diethylazoxycinnamate (DEAC) in their different phases. As in the case of nematic compounds,²⁻⁵ we have observed changes in the spectra when the smectogens undergo phase transitions. In particular, we have found for the first time in smectic compounds a low frequency intermolecular mode exhibiting both frequency shift and intensity change at the transitions.

The experimental arrangement consisted of a photon counting setup⁵ used in conjunction with a double monochromator. The exciting light was the 5145 Å line of Ar⁺ laser. By employing the iodine filter technique,⁷ we were able to obtain Raman spectra to within 5 cm⁻¹ of the laser line. To insure proper temperature control, a copper block immersed in an oil bath was used. The temperature was monitored constantly and fluctuations were less than 0.035°C. All solid samples were investigated in the polycrystalline form.

In the spectral range of 5 to 100 cm⁻¹, solid DEAB and DEAC have a single Raman mode at 22 cm⁻¹ and 26 cm⁻¹ respectively (see Fig. 1). This Raman mode shows significant changes as the material undergoes phase transitions. In the transition from solid to smectic, it shifts to 14 cm⁻¹ (for both compounds) and decreases in intensity significantly. Then, as the isotropic phase is reached, it vanishes abruptly. In Fig. 2 we have plotted the frequency shift as a function of temperature for DEAB. The curve exhibits a characteristic quasidiscontinuity at both transitions.

Figure 3 shows the change in the mode intensity as temperature changes. The discontinuities at both the solid-smectic and the smectic-isotropic transitions are observed. The

linewidth of this mode remains unchanged in the solid and smectic phases. DEAC shows similar behavior.

To explain our results qualitatively, let us first consider the structure of smectic compounds as deduced from X-ray work.^{8,9} In the solid phase, the unit cell is triclinic and contains two molecules. The molecules, which are nearly planar, are fixed in position and packed with the planes of adjacent molecules facing each other in a parallel array. This is in contrast with the imbricated structure of nematogenic substances. The carboxyl and azoxy groups of DEAB are found to be in the cis configuration. This implies the existence of strong dipole moments in the plane of the molecule and at angles to its long axis. In the smectic phase, the thickness of the molecular layers increases over that of the solid lattice,⁹ but the long axis of the molecules remains preferentially aligned. The molecules can now move more randomly within the layers, and presumably can have hindered rotation about their long axes.¹⁰ Finally, in the isotropic phase, complete disorder sets in and the molecules undergo random motion in all dimensions.

We interpret the origin of the observed low frequency mode as arising from the intermolecular dipole-dipole interaction between the carboxyl groups of two molecules in adjacent layers. This conclusion is supported by the fact that the frequency of this mode is nearly independent of the length of the end groups. As temperature increases and the smectic phase is reached, the interaction between layers is weakened¹⁰ when the spacing between them increases. This explains the observed shift of the phonon mode to a lower frequency

(somewhat similar to the change of a lattice mode in response to structural change in the first-order phase transition of a solid). The observed drop in intensity can also be explained in terms of the weaker intermolecular interaction due to a larger spacing between layers, and the newly attained rotational freedom in the smectic phase. That the molecules acquire such rotational freedom in the smectic A phase is supported by the significant increase (40-50%), which we observed, in the linewidth of the high frequency modes. In the isotropic liquid, the breakdown of order results in a very small number of pairs of molecules which interact with a definite configuration through the carboxyl groups, and hence the low-frequency Raman mode disappears.

In the spectral region of 100 to 2000 cm^{-1} , we observed around 30 strong Raman lines (as compared with 13 lines reported by Zhdanova et al.⁴) of the same order of intensity as the 992 cm^{-1} line of pure benzene. As the samples changed phase from solid to smectic and to isotropic, most of the lines broaden and some decrease in intensity. However, no frequency shift was detectable in any of these lines. Our complete Raman spectra of the homologous members of DEAB and DEAC in the three phases will be published elsewhere.

We have also investigated the Raman spectra of some smectic members of the homologous series of azoxybenzene and found no low frequency modes. The end groups of these compounds have larger molecular weights. One should therefore predict a much smaller frequency for the intermolecular mode. This is consistent with our observation.

A quantitative analysis of the results using a simple phase-transition model will be initiated in order to gain better understanding of the results.

ACKNOWLEDGEMENT

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FIGURE CAPTIONS

Fig. 1. Low frequency Raman spectra of DEAB in the three phases:

(a) solid phase at room temperature; (b) smectic phase at $T = 114.7^{\circ}\text{C}$; (c) liquid phase at $T = 124.1^{\circ}\text{C}$. The slit width is 1.5 cm^{-1} .

Fig. 2. Temperature dependence of the shift of the 22 cm^{-1} mode of DEAB.

Fig. 3. Temperature dependence of the integrated intensity of the 22 cm^{-1} mode of DEAB.

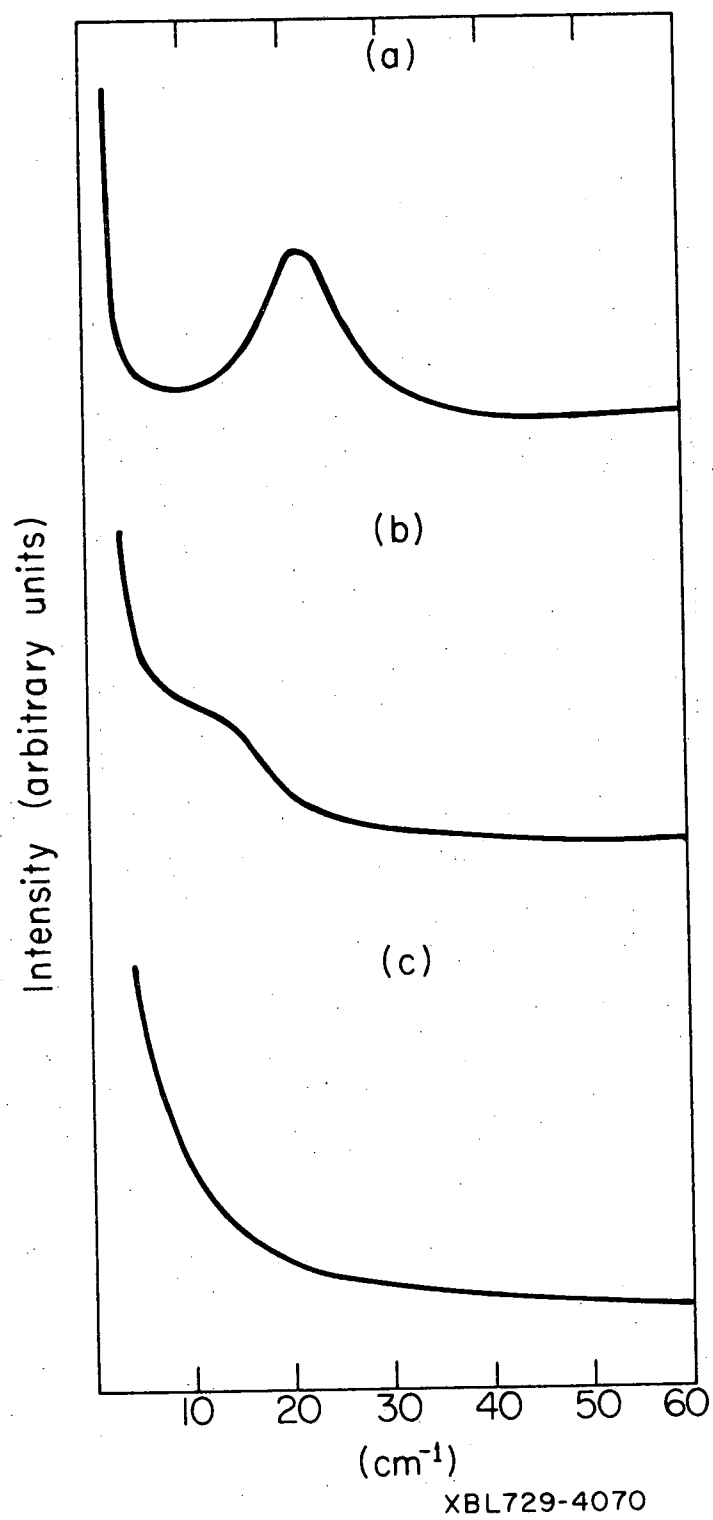
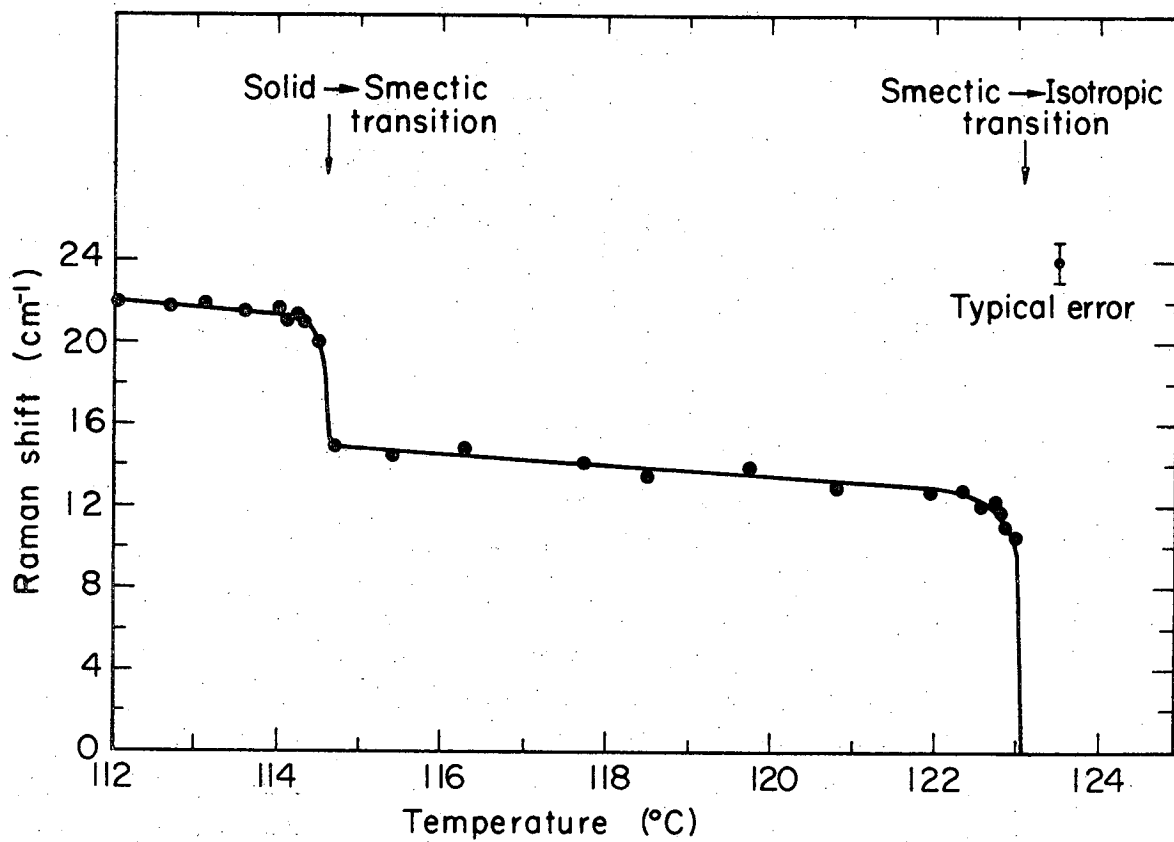


Fig. 1



XBL 728-3782

Fig. 2

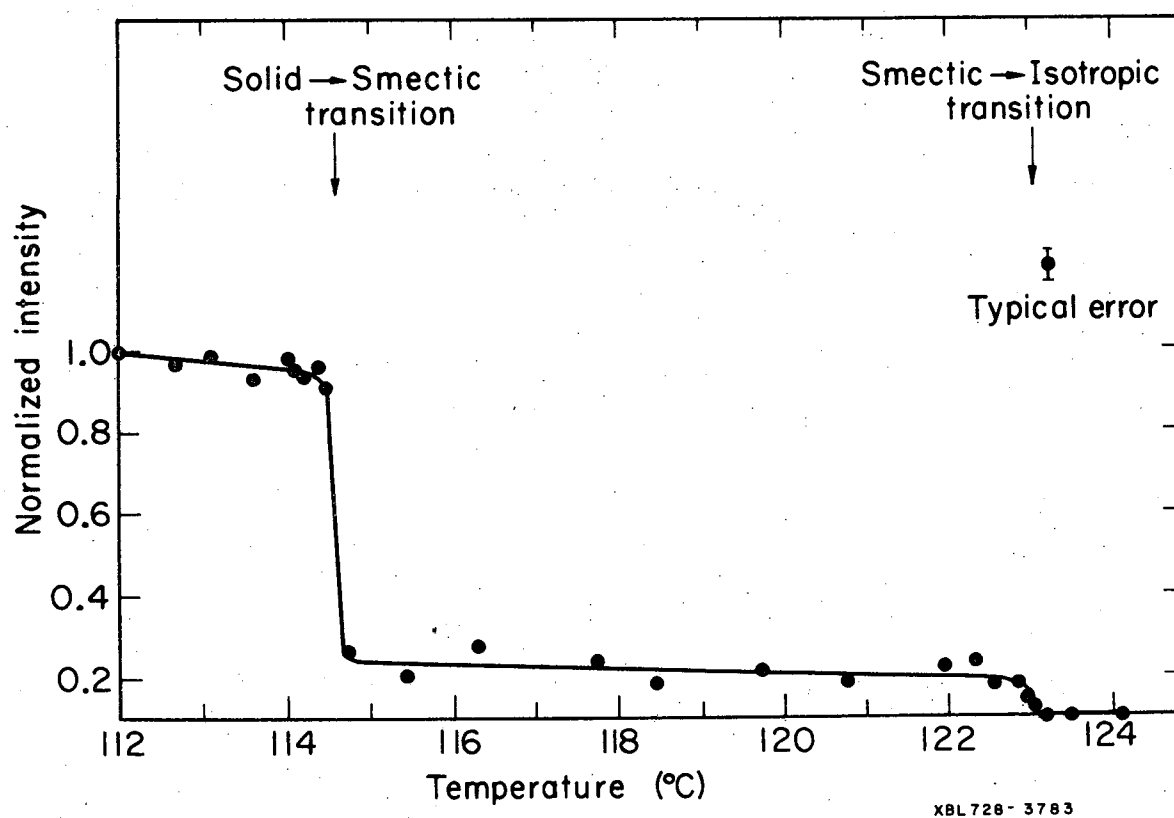


Fig. 3

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